APPENDIX I.

APPLICATION WORK ORDER

COUNTY 13

STOKER COMPANY
3390 DOGWOOD RD. IMPERIAL, CA. 92251 (619) 355-1161

WORK ORDER

NOTICE OF INTENT TO APPLY RESTRICTED MATERIALS [ ] AND / OR RECOMMENDATION [X]

WORK ORDER [redacted]

GROWER:	PERMIT:	TIME:	DATE:
MAGCO	13-95-130072A	02:00 PM	01-1

LOCATION:	SEC	TWN	RNG	M
ASH 154	8	16S	15E	S

ACRES:	CROP:
28	ONIONS

APPLICATION INSTRUCTIONS:
HOLD

METHOD: GROUNI
VOLUME PER ACRE:
TOTAL VOLUME:

SUPPLIER:	INVOICE:	JOB RECOMMENDATION	OTHER REFERENCE
STOKER CO.		2745	ASH 154

PESTS:
WEEDS

RATE PER ACRE	CHEMICAL	TOTAL
1.0000 PT	BUCTRIL 33.4% AI.	3-1/2 GAL
	40 GAL/AC	
	8 row rig 80 gal appl	

SPECIAL INSTRUCTIONS:

40" BEDS FULL COVERAGE

3 Cent 1/2 if possible

REENTRY:
24 HRS / DAYS XX
XXX AFTER DRIFT & VAPOR GONE
XXX AFTER SPRAY DRIES
RESTRICTIONS: 9 Completed Hybrid 9
___ DAYS TO HARVEST 60
7 DAYS TO PASTURE 106 -
DO NOT FEED OR GRAZE LIVESTOCK ON CROP WASTE FOR ___ DAYS 4-00
XXX AVOID DRIFT TO SURROUNDING AREAS
XXX TOXIC TO BIRDS, BEES, FISH AND WILDLIFE

[ ] A WRITTEN RECOMMENDATION HAS NOT BEEN MADE COVERING THE APPLICATION OF THE MATERIAL COVERED BY THIS WORK ORDER.

STEVE FINNELL	FILED: [ ]	DATE:	TIME:	
COMPLETED: AM - PM - NIGHT	TACH TIME:	LOADS:	TEMP:	WIND:
PILOT:	CREW:	TANKER:	FLAGGERS:	

APPENDIX II

SAMPLING PROTOCOL

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Bromoxynil Application Monitoring in Imperial County During the Winter of 1995

Engineering and Laboratory Branch

Monitoring and Laboratory Division

Project No. C87-117A

Date: December 12, 1994

APPROVED:

Don Fitzell, Project Engineer

Peter K. Ouchida, Manager
Testing Section

Peter K. Ouchida for
George Lew, Chief
Engineering and Laboratory Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Bromoxynil Application Monitoring in Imperial County
During the Winter of 1995

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will conduct a 3-day source directed ambient monitoring program for bromoxynil in Imperial County. The monitoring results will be used by DPR to decide if bromoxynil should be identified as a toxic air contaminant. This monitoring will occur prior to, during, and following an application of this pesticide. Bromoxynil is a selective herbicide used on a wide variety of crops. Peak use in California occurs during the winter months for wheat grown in Imperial County.

Bromoxynil is not regulated as a restricted use material under Section 6400, Title 3 of the California Code of Regulations. It is, however, a Category II pesticide and subject to the provisions of the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65).

The results from a similar monitoring program conducted in 1993 were found to be not representative due to the placement of the monitors and unusual wind patterns. At that time (and all previous pesticide monitorings) samplers were located upwind and downwind of the field based on prevailing winds. With the approval of the DPR we have since that time surrounded the field by placing a sampler on each side of the field.

II. Sampling

Background samples will be taken to establish if bromoxynil is present prior to application. One meteorological station will be set up to determine wind speed and direction prior to, during, and after application of bromoxynil. Samples will be collected with XAD-2 tubes using battery powered pumps capable of flows of approximately 2 liters per minute (ATTACHMENT I). Four samplers will be used; one on each side (assuming a rectangular field) of the field at a distance of approximately 15 yards. These distances are approximate and dependent on the physical obstacles surrounding the field. As closely as feasible, the sample tubes will be changed according to the schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" (ATTACHMENT II). All samples will be stored in an ice chest or refrigerator until analysis. ARB staff will transport the samples to Sacramento for analysis.

Calibrated rotometers will be used to control sample flow rates. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data, including field size, application rate, formulation, and method and length of application. A copy of the "Notice of Intent" will be included when available.

III. Analysis

The samples will be analyzed by ARB staff at the Sacramento laboratory. Samples will be analyzed by gas chromatography using an electron capture detector (ECD). The sample is desorbed with 2.0 ml ammonical methanol, acidified and extracted with toluene. The phenol is then reacted with diazomethane to form the methyl ester derivative. The analytical procedure is fully described in ARB's NLB 026, "Method for the Determination of Bromoxynil and Bromoxynil Esters in Ambient Air" (ATTACHMENT III).

IV. Quality Assurance

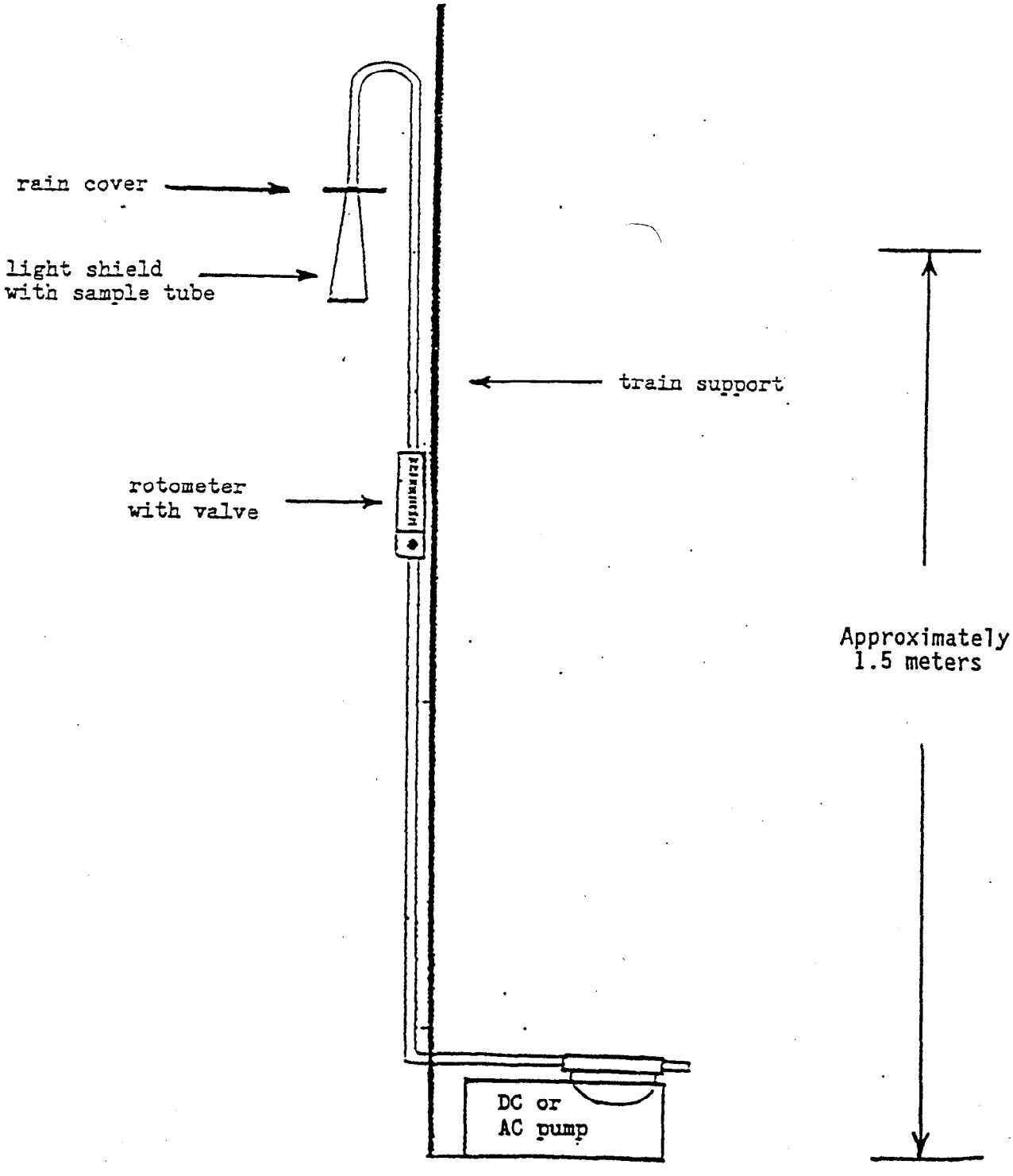
Procedures will follow ARB's "Quality Assurance Plan for Pesticide Monitoring." The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Sample flow rates will be calibrated prior to and after sample collection. Field blanks will be provided and every effort will be made to obtain field spikes.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers (Instrument Technician).

ATTACHMENT I

PESTICIDE MONITORING APPARATUS


rain cover
light shield
with sample tube
train support
rotometer
with valve
DC or
AC pump
Approximately
1.5 meters

ATTACHMENT II

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN

FOR PESTICIDE MONITORING

Prepared by the

Monitoring and Laboratory Division

and

Stationary Source Division

Revised: February 4, 1994

APPROVED:

Geneviève Shiroma, Chief
Toxic Air Contaminant
Identification Branch

_____, Chief
Quality Management and Operations
Support Branch

_____, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signifiy that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method.

5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

   A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

   Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

   The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

   Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

   The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

   All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

ATTACHMENT III

BROMOXYNIL S.O.P. (GC/ECD)

METHOD NLB026

METHOD FOR THE DETERMINATION OF BROMOXYNIL AND BROMOXYNIL ESTERS IN AMBIENT AIR

1. SCOPE

This document describes a method for the sampling and analysis of bromoxynil (2,4-dibromo-hydroxybenzonitrile) and bromoxynil esters at concentrations normally expected in ambient air. The method was developed from the work of Crouch and Pullin (Pestic. Sci., 5, pg 281, 1974).

2. SUMMARY OF METHOD

After sampling using a low-volume system comprising a sample pump, calibrated flow controller, and purified XAD-2 sorbent trap, the exposed XAD-2 resin is desorbed with 2.0 ml. ammonical methanol, acidified, and back extracted with toluene. The phenol is then reacted with diazomethane to form the methyl ether derivative. Two microliters are injected into a gas chromatographic system equipped with a splitless injector, DB-1 capillary column, and electron capture detector. The resultant peak is identified by a characteristic retention time and quantitated in reference to external standards.

3. INTERFERENCES/LIMITATIONS

Components having similar GC retention times will interfere, causing misidentification and/or erroneous quantitation. Positive results are confirmed using a DB-1301 capillary column.

4. APPARATUS

4.1 Perkin-Elmer Model 8500 Gas Chromatograph/ECD/Data System.

4.2 DB-1 fused silica capillary column, 30 meters X 0.35 mm i.d., 0.25 micron film thickness.

4.3 Amber vials, 3.7 ml capacity, with teflon-lined septum caps.

4.4 Sample agitator with timer.

4.5 XAD-2 glass absorption tubes, containing 400 mg in primary section, 200 mg in secondary section.

4.6 Millimolar diazomethane generator, Pierce #28131, or equiv.

5. REAGENTS

5.1 Ammonical Methanol: Mix 10 ml. concentrated ammonium hydroxide with 190 ml methanol. Store in amber glass container.

5.2 Toluene, Pesticide Grade, or equivalent.

5.3 Diazomethane Reagent: CAUTION: DIAZOMETHANE IS EXTREMELY TOXIC AND CAN EXPLODE AT HIGH TEMPERATURES OR IF SUBJECTED TO SHOCK. AVOID GROUND GLASS JOINTS. USE EXTREME CAUTION AND WEAR GLOVES. PREPARE IN FUME HOOD.
Place 100 mg of N-methyl-N-nitroso-N'-nitroguanidine into the inside tube of the millimolar generator. Add 0.5 ml water. Place 3 ml diethyl ether in the outside tube and assembly the generator. Insert the lower part of the generator into an ice bath. Using a 1 ml syringe, inject 0.6 ml of 5N sodium hydroxide through the septum into the inside tube. INJECT THE SODIUM HYDROXIDE SOLUTION SLOWLY, AS THERE WILL BE A PRESSURE BUILD-UP. Let the generated diazomethane accumulate in the cold ether for 45 minutes. Carefully disassemble the apparatus and transfer the ether/diazomethane solution to a 5 ml amber glass screw-capped vial with teflon septum. Keep refrigerated. This reagent is good for one week.

5.3 Stock Standard: 1000 ug/ml: Dissolve 0.100 gram bromoxynil (Chem Service, 99+%) in 100 ml Pesticide Grade toluene.

5.4 Calibration Standard: 1.0 ug/ml: dilute 100 ul of Stock Standard to 100 ml with toluene.

6. INSTRUMENT CONDITIONS

Column: 30m X 0.35 mm i.d. DB-1 fused silica capillary column

Temperature: Injector: 300 C
Detector: 350 C
Oven: 60 C initial, hold for 1 min; ramp ballistically to 140 C, hold for 1 min; ramp at 5 C/min to 260 C, hold for 5 min.

Detector: ECD

Flow Rates: Carrier: He at 25 cm/sec; 30 cc/min at splitter, 0.7 min. splitless hold. 60 cc/min Nitrogen detector make-up gas.

7. ANALYSIS PROCEDURE

7.1 Calibration standards and solvent blanks must be analyzed in the same manner as samples. The calibration standards, 1.0 ug/ml and 0.1 ug/ml in toluene, are derivatized with diazomethane along with each batch of samples analyzed.

7.2 After removal of the red end caps of the XAD-2 tubes, the tube is scored with a glass cutter above the location of the retainer spring. The glass wool plug and the primary section (400 mg) is placed in a 3.7 ml amber glass vial. The secondary section is retained for later analysis if the results of the primary section are positive. Make sure that all vials are properly identified.

7.3 Place 2.0 ml of the ammonical methanol solution in the vials and place on agitator for 90 minutes. Remove 1.0 ml of the extract and place in a 15 ml screw-capped centrifuge tube. Allow to stand for 2 hrs.

7.4 Add 1 ml of aqueous 6N hydrochloric acid, mix, and add 4.0 ml of Pesticide Grade toluene. Shake for one minute and allow the phases to separate. Repeat the extraction. Remove 2.0 ml of the toluene extract and place in an amber screw-capped glass vial.

7.5 Add 100 ul of the diazomethane/ether solution to toluene extracts, calibration standards, and solvent blank. Mix and allow to stand overnight.

7.6 Inject 2.0 ul of the standards, blanks, and sample extracts into the gas chromatographic system using Grob splitless technique. Compare the results of the analysis of the calibration standards to previous analyses to insure consistent response. The total mass of bromoxynil per sample is calculated as follows:

$$\text{ug/sample} = \frac{\text{Stnd Conc. X Sample Area Count X 8}}{\text{Stnd Area Count}}$$

8. METHOD SENSITIVITY AND PRECISION

Method sensitivity and precision are outlined in Table 1. The data was generated using standards.

9. DESORPTION EFFICIENCIES AND SAMPLE STABILITY

Desorption efficiencies and sample stability data is listed in Table 2.

TABLE 1
METHOD SENSITIVITY AND PRECISION FOR BROMOXYNIL

CONCENTRATION, UG/ML	AREA COUNT	RELATIVE STND. DEV. n=4
1.0 ug/ml	16.234	5.2 %
0.5 ug/ml	8.112	4.4 %
0.1 ug/ml	1.579	8.0 %
0.02 ug/ml	0.322	8.8 %

Correlation coefficient: 0.999 Slope: 0.0615 ug/ml/ AC
Intercept: 0.0014 ug/ml LOD : 0.0020 ug/ml (0.016 ug/sample)

TABLE 2
DESORPTION EFFICIENCIES AND STORAGE STABILITY

BROMOXYNIL, UG/SAMPLE*	RECOVERED(n=3)	RECOVERED AFTER 7 DAYS(n=3)
2.0 ug/sample	1.86 (93%)	1.91 (96%)
1.0 ug/sample	0.88 (88%)	0.92 (92%)
0.4 ug/sample	0.38 (95%)	0.36 (90%)

*Note: Bromoxynil was spiked onto the primary section of XAD-2 tubes using microliter syringes and allowed to equilibrate for 1 hour. Three tubes were analyzed immediately; three tubes were stored at -4 C for seven days and then analyzed.

APPENDIX III

ANALYTICAL S.O.P. (HPLC)

STATE OF CALIFORNIA
AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

S.O.P. NO. MLD 026

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF BROMOXYNIL IN AMBIENT AIR

1.0 SCOPE

This is a high performance liquid chromatographic (HPLC) method for the determination of bromoxynil in ambient air utilizing solid adsorbent. The method was developed from the U.S. EPA Method 1661.

2.0 SUMMARY OF METHOD

XAD-2 tubes are used to collect ambient air samples containing bromoxynil. The primary resin of the XAD-2 is extracted with acetone by shaking the mixture for 1.5 hours. An aliquot of the supernatant extract (0.75 mL) is placed in a vial and evaporated. The contents of the vial are immediately diluted with 0.75 mL of HPLC grade water. The aqueous solution is then analyzed by reverse-phase (C-18) HPLC with UV detection (280 nm). The presence of bromoxynil is confirmed by analysis at a second wavelength (255 nm).

3.0 CONTAMINATION AND INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running method blanks.

3.2 Glassware and, where possible, reagents are cleaned by rinsing with solvent and baking at 450°C for 1 hour minimum in a muffle furnace or kiln. Some thermally stable materials may not be eliminated by this treatment and thorough rinsing with acetone and pesticide-quality acetonitrile may be required.

3.3 Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled.

4.0 APPARATUS

4.1 A Waters gradient HPLC system consisting of mobile phase reservoirs; high pressure pumps; and injection valve or automatic sampler; a Nova-Pak C-18 reverse phase column 3.9 mm × 15 cm; a variable wavelength UV detector operating at 280 nm; and a data system.

4.2 Supelco 4 mL glass desorption vials with Teflon lined screw caps. Sun brokers 1 mL autosampler "Sun Vial" with polyethylene cap septum.

4.3 Sample shaker/desorber and sample racks.

4.4 Filtration and degassing system for mobile phase solvents such as Waters Part #85124.

4.5 Various volumetric pipets and flasks and graduated cylinders.

4.6 Vacuum oven with the capability to heat to 50°C and pull vacuum of -10" Hg vacuum.

4.7 Polyethlene gloves - used to handle various chemicals.

5.0 REAGENTS

5.1 Solvent: HPLC grade acetone and acetonitrile (Pesticide Quality).

5.2 Reagent water: HPLC grade water in which the compounds of interest and interfering compounds are not detected by this method.

5.3 Standard: Bromoxynil was obtained from Chem Service.

5.4 Potassium dihydrogen phosphate (ACS).

5.5 HPLC Mobile Phase: Dissolve 1.361 g of potassium dihydrogen phosphate into 1000 L of HPLC grade water. Mix thoroughly.

6.0 CALIBRATION

6.1 Establish the HPLC operating conditions equivalent to those in Table 1 (see page 6).

6.2 Stock Standard: Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 10 mg bromoxynil in a 100 mL ground-glass stoppered volumetric flask and fill to the mark with methanol. After the bromoxynil is completely dissolved, transfer the solution to a 150 mL vial with PTFE-lined cap.

6.3 Prepare working standards with concentrations of 100, 600 and 3,000 μg/L using HPLC water as solvent.

6.4 Prepare a control sample with a concentration of 700 μg/L.

6.5 Equilibrate column for 30 minutes at initial startup for the day. Analyze a blank to check for method interference.

6.6 Calibrate the instrument using the three working standards.

6.7 Check the calibration of the instrument by analyzing a control sample (700 μg/L). The calculated concentration should be $\pm$10% of the actual concentration.

7.0 ANALYSIS OF SAMPLES

7.1 The field samples are collected on XAD-2 resin air sample tubes which are refrigerated after exposure and before extraction.

7.2 Remove the glass wool from the primary end of an XAD-2 tube with forceps and place it into a 4.0 mL vial. Pour the XAD-2 resin into the vial and add 3.0 mL of acetone. Retain the secondary section of the XAD-2 tube for later analyses in case the primary section gives a positive result.

7.3 Agitate the capped vial for 1.5 hours. Take 0.75 mL of the supernatant extract and place into a 1 mL autosampler vial. Evaporate the solution in a vacuum oven set at 50°C and -10" Hg vacuum. The contents of the vial are then immediately diluted with 0.75 mL of HPLC grade water.

7.4 Analyze a blank with each sample set. Analyze a control sample immediately after the working standards, and every ten samples thereafter, to check the linearity and validity of the calibration curve.

7.5 Results are recorded in micrograms per sample and are calculated as:

$$\mu g = \mu g/L \text{ (found)} \times 0.003L$$

8.0 METHOD LIMIT OF DETECTION (LOD)

Six replicates of a solution with a concentration of 50 μg/L were analyzed. The following are the calculated concentrations.

Sample Name	Concentration (μg/L)
Replicate 1	50.3
Replicate 2	62.3
Replicate 3	62.3
Replicate 4	51.9
Replicate 5	54.8
Replicate 6	54.6

mean = 56.0 μg/L
std. dev. = 5.13 μg/L = 0.00513 μg/mL
LOD = 3 × STD. DEV. = 0.015 μg/mL
LOD = 0.045 μg/tube.

9.0 QUALITY CONTROL INFORMATION

9.1 Nine XAD-2 tubes were spiked at different concentration levels. The tubes were extracted and analyzed the following day.

Sample Name	Spike Amt., μg	Spike Rec., μg	% Recovery
A1	0.23	0.22	96
A2	0.23	0.22	96
A3	0.23	0.23	100
A4	0.56	0.51	89
A5	0.56	0.51	89
A6	0.56	0.56	97
A7	1.15	1.03	90
A8	1.15	1.06	92
A9	1.15	1.08	94

9.2 Trip spikes and blank were analyzed with field samples and the following results were obtained:

Sample Name	Spike Amt., μg	Spike Rec., μg	% Recovery
SP-1	0.58	0.50	86
SP-2	1.72	1.80	105
SP-3	2.88	2.79	97
SP-4	0.00	<0.04	---

10.0 COLLECTION/CONVERSION EFFICIENCY (Results republished from Revision 0)

Bromoxynil was spiked onto the primary sections of XAD-2 sampling tubes at the concentrations indicated and allowed to equilibrate overnight. The sampling tubes were then connected to a sampling pump and air was drawn through the tubes as a rate of 2 liters/minute for a period of twenty-four hours. The resultant samples were then analyzed according to Standard Operating Procedure MLD026, Revision 0. The results of the collection/conversion study are listed below:

Bromoxynil, μg Spiked	Recovered, μg (Primary, n=3)	Recovered, μg (Seconary, n=3)
4.00	2.72	0.38 (9.5%)
2.00	1.48	0.08 (4.0%)
1.00	0.62	<0.02
Blank	<0.02	<0.02

TABLE 1

HPLC Chromatographic Conditions

Column: Waters Nova-Pak C-18, 3.9 mm x 150 mm

Pre-column: Waters Guard-Pak (Nova-Pak C-18)

Flowrate: 1.0 mL/min

Injection volume: 20 μl

Detector: UV detector set at 280 nm for quantitation. 255 nm for confirmation. Retention time is 4.8 minutes for bromoxynil.

Mobile Phase A: HPLC grade acetonitrile.

Mobile Phase B: 0.01 M KH_2PO_4 in HPLC grade water.

Gradient Program:

Time	%A	%B
0.0	50	50
4.0	50	50
4.5	100	0
5.0	100	0
5.5	50	50
20.0	50	50

APPENDIX IV

CIMIS WEATHER DATA

California Irrigation Management Information System - Department of

Daily Data for Station # 53

DATE	HOUR	STD	EXPER PRECIP	EXPER SOLAR	RADIATION NET	VAPOR PRESSURE	AIR TEMP	RELATIVE HUMIDITY	DEW-POINT	WIND SPEED	WIND DIR
			#1	#2							
		in.	in.	---Ly/day---		mBars	F	%	F	mph	(0-360)
1/19/95	1	0.00	0.00	-1	-75	6.01	39.7	72	31.6	1.5	343
38.9		64.4	72.40	72.40							
	2	0.00	0.00	-1	-73	6.38	38.4	81	33.1	2.2	203
34.9		64.2	81.10	81.10							
	3	0.00	0.00	-1	-73	6.31	37.9	82	32.8	2.5	279
29.6		63.9	81.80	81.80							
	4	0.00	0.00	-1	-73	5.96	37.2	79	31.4	2.4	296
27.0		63.7	79.20	79.20							
	5	0.00	0.00	-1	-73	6.16	37.9	80	32.2	2.2	198
28.3		63.8	79.90	79.90							
	6	0.00	0.00	-1	-73	6.06	36.9	82	31.8	2.1	248
36.6		63.3	81.50	81.50							
	7	0.00	0.00	8	-67	6.14	36.9	83	32.1	2.2	252
42.1		63.1	82.90	82.90							
	8	0.00	0.00	169	33	6.64	40.3	78	34.1	2.4	266
35.9		62.9	78.10	78.10							
	9	0.00	0.00	371	120	8.27	46.8	76	39.6	2.8	267
24.2		62.8	76.00	76.00							
	10	0.01	0.00	783	355	7.94	53.1	54	38.6	2.9	212
18.0		62.7	54.08	54.08							
	11	0.01	0.00	864	425	6.48	61.5	35	33.5	2.6	257
26.1		62.7	34.86	34.86							
	12	0.01	0.00	983	506	6.20	63.4	31	32.4	2.8	272
29.6		62.9	31.14	31.14							
	13	0.01	0.00	1023	530	5.18	64.9	25	28.0	4.7	335
24.0		63.1	24.62	24.62							
	14	0.01	0.00	769	365	4.80	65.1	23	26.1	3.2	309
34.4		63.4	22.71	22.71							
	15	0.01	0.00	690	311	4.71	65.7	22	25.7	3.1	312
41.0		63.8	21.85	21.85							
	16	0.00	0.00	305	94	5.71	64.6	27	30.3	1.6	240
23.1		64.1	27.49	27.49							
	17	0.00	0.00	95	15	6.42	61.4	35	33.2	1.5	197
19.3		64.4	34.44	34.44							
	18	0.00	0.00	1	-51	7.56	56.6	48	37.3	2.1	213
10.1		64.6	49.00	49.00							
	19	0.00	0.00	0	-49	8.31	52.6	61	39.8	2.0	241
14.6		64.7	61.50	61.50							
	20	0.00	0.00	0	-49	7.49	49.5	62	37.1	3.3	230
8.8		64.7	62.24	62.24							
	21	0.00	0.00	0	-51	6.51	49.5	54	33.6	1.9	180
26.2		64.6	53.91	53.91							
	22	0.00	0.00	0	-50	6.56	46.3	61	33.8	1.7	100
48.5		64.5	61.50	61.50							
	23	0.00	0.00	0	-48	6.91	43.2	73	35.1	1.9	194
51.4		64.4	72.70	72.70							

PERIOD 1/19/95 - 1/19/95

[illegible]	[illegible]	[illegible]	-1	[illegible]	[illegible]	[illegible]	[illegible]	32.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	73.10
2	0.00	0.00	-1	-151	[illegible]	44.2	[illegible]	35.2	2.3	232	[illegible]	[illegible]	70.50	70.50
3	0.00	0.00	-1	-145	7.74	42.6	83	37.9	1.7	261	[illegible]	67.7	83.40	83.40
4	0.00	0.00	-1	-149	6.83	41.0	78	34.8	3.2	248	29.4	63.6	78.40	78.40
5	0.00	0.00	0	-150	6.27	39.6	76	32.6	1.6	40	41.6	63.4	75.80	75.80
6	0.00	0.00	0	-148	6.37	38.4	81	33.0	1.4	117	46.7	63.3	81.00	81.00
7	0.00	0.00	11	-141	6.09	37.2	81	31.9	2.0	109	41.9	[illegible]	80.90	80.90
8	0.00	0.00	257	14	6.92	41.3	78	35.1	2.2	221	47.0	62.9	78.40	78.40
9	0.00	0.00	666Y	192	6.47	53.5	46	33.4	1.0	222	42.9	62.7	46.21	46.21
10	0.01	0.00	925	353	5.46	57.3	34	29.2	2.7	64	53.4	62.1	33.77	33.77
11	0.01	0.00	1245	570	4.92	62.3	26	26.7	5.2	89	17.9	62.6	25.76	25.76
12	0.02	0.00	1381	665	4.84	65.4	23	26.3	5.0	109	31.7	62.8	22.64	22.64
13	0.02	0.00	1225	639	4.48	66.3	20	24.5	5.0	109	26.8	63.1	20.30	20.30
14	0.01	0.00	942	474	4.47	66.2	20	24.4	5.5	96	21.0	63.5	20.39	20.39
15	0.01	0.00	861	409	4.90	66.7	22	26.6	5.2	111	25.8	63.9	21.91	21.91
16	0.01	0.00	502	192	4.93	65.7	23	26.8	4.6	115	11.1	64.2	22.80	22.80
17	0.00	0.00	130	15	6.46	61.9	34	33.4	3.3	98	11.6	64.5	34.43	34.43
18	0.00	0.00	1	-74	7.28	54.1	51	36.4	1.9	128	16.8	64.7	51.13	51.13
19	0.00	0.00	0	-75	6.45	50.4	52	33.4	2.0	80	34.8	64.8	51.71	51.71
20	0.00	0.00	0	-74	6.62	48.6	57	34.0	2.6	160	70.2	64.7	57.04	57.04
21	0.00	0.00	0	-74	6.49	48.1	57	33.5	1.3	155	68.4	64.6	56.82	56.82
22	0.00	0.00	-1	-73	6.67	48.3	58	34.2	3.0	188	48.5	64.5	58.02	58.02
23	0.00	0.00	-1	-73	6.82	48.7	58	34.7	2.2	213	43.4	64.4	58.47	58.47
24	0.00	0.00	-1	-75	6.69	51.8	51	34.3	2.6	246	55.1	64.3	51.08	51.08

1/20/95 0.08 = TOTAL ETo

1 calorie/sq.cm/day (Ly/day)*.484=W/sq.m inches*25.4=mm (F-32)*5/9=C

mph*.447=m/s mBars*.1=kPa

------------------------------ SEVERE FLAGS ------------------------------

INFORMATIVE FLAGS ---------------------

C -not collected N/A -not available noc -cannot calculate Y -out of range

-all quality control not performed

S -not in service R -out of range I -ignore,no meaning F -estimated

* * * * PRELIMINARY DATA * * * * note: TOTAL ETo = sum of hourly ET

California Irrigation Management Information System - Department of Water Resources

Hourly Weather Data for Station # 68 Seeley

DATE	HOUR	ETo (in.)	PRECIP (in.)	SOLAR RADIATION (Ly/day)	NET RADIATION (Ly/day)	VAPOR PRESSURE (mBars)	AIR TEMP (F)	RELATIVE HUMIDITY (%)	DEW POINT (F)	WIND SPEED (mph)	WIND DIR (0-360)	RES WIND DIR	SOIL TEMP (F)	EXPER #1	EXPER #2
1/[illegible]1/95	1	0.00	0.00	-1	-100	6.98	52.6	52	35.3	2.1	209	32.2	64.2	51.92	51.92
	2	0.00	0.00	-1	-97	7.59	51.5	58	37.4	3.3	114	13.0	64.1	58.59	58.59
	3	0.00	0.00	-1	-92	8.85	49.7	73	41.4	3.5	108	14.5	64.1	73.00	73.00
	4	0.00	0.00	-1	-91	9.18	49.7	76	42.3	3.4	105	35.5	64.0	75.60	75.60
	5	0.00	0.00	-1	-91	9.51	49.7	78	43.2	3.1	345	42.4	64.0	78.50	78.50
	6	0.00	0.00	-1	-89	10.05	49.9	82	44.7	3.7	31	24.9	64.0	82.10	82.10
	7	0.00	0.00	3	-88	10.05	50.5	80	44.7	5.1	23	30.9	64.0	80.20	80.20
	8	0.00	0.00	70	-45	10.33	51.0	81	45.4	2.5	357	58.3	63.9	81.20	81.20
	9	0.00	0.00	451	157	10.78	53.4	77	46.5	2.7	247	23.7	63.9	77.60	77.60
	10	0.01	0.00	972	413	10.37	58.4	62	45.5	2.6	236	31.4	64.0	62.29	62.29
	11	0.01	0.00	1143	527	9.73	61.3	52	43.8	2.8	281	34.0	64.1	52.55	52.55
	12	0.01	0.00	1360	679	8.83	63.4	44	41.3	3.7	290	44.2	64.3	44.30	44.30
	13	0.01	0.00	1331	649	7.70	65.2	36	37.8	5.1	333	36.3	64.6	36.27	36.27
	14	0.01	0.00	902	456	7.13	65.5	33	35.9	5.8	358	22.7	65.0	33.22	33.22
	15	0.01	0.00	506	207	7.89	64.8	38	38.4	7.4	25	18.4	65.4	37.72	37.72
	16	0.00	0.00	285	83	9.04	62.9	46	41.9	7.1	33	12.5	65.7	46.14	46.14
	17	0.00	0.00	89	-15	9.20	61.0	50	42.4	6.2	20	9.4	66.0	50.20	50.20
	18	0.00	0.00	1	-38	8.82	57.2	55	41.3	2.9	3	35.7	66.1	55.24	55.24
	19	0.00	0.00	0	-37	9.88	53.3	71	44.2	2.9	262	58.4	66.2	71.20	71.20
	20	0.00	0.00	0	-37	9.78	54.2	68	44.0	1.9	187	34.4	66.2	68.33	68.33
	21	0.00	0.00	0	-37	9.57	54.7	66	43.4	2.2	195	23.2	66.1	65.53	65.53
	22	0.00	0.00	0	-37	9.29	51.9	71	42.6	1.7	14	70.3	66.0	70.50	70.50
	23	0.00	0.00	0	-37	9.15	49.6	76	42.2	2.0	289	43.8	65.9	75.70	75.70
	24	0.00	0.00	0	-36	8.92	46.9	82	41.6	1.3	94				

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	85.	81.30	81.30							
	2	0.00	0.00	0	-85	8.43	44.8	84	40.1	2.4	242
13.0	85.5	83.40	83.40							
	3	0.00	0.00	-1	-86	7.85	42.9	84	38.3	2.3	295
47.5	85.3	83.50	83.50							
	4	0.00	0.00	-1	-85	7.96	43.2	84	38.7	2.2	258
44.6	85.1	83.90	83.90							
	5	0.00	0.00	-1	-86	8.06	43.8	83	39.0	1.9	183
33.7	84.9	82.90	82.90							
	6	0.00	0.00	-1	-86	7.82	42.8	84	38.2	1.4	103
53.5	84.7	83.50	83.50							
	7	0.00	0.00	18	-72	7.56	41.6	85	37.3	2.2	263
26.8	84.5	84.50	84.50							
	8	0.00	0.00	220	54	8.48	44.8	84	40.3	1.5	221
36.7	84.3	83.90	83.90							
	9	0.00	0.00	436	152	9.80	51.2	76	44.0	1.2	213
51.6	84.2	76.40	76.40							
	10	0.01	0.00	749	346	9.52	56.2	62	43.3	2.6	304
17.7	84.1	61.82	61.82							
	11	0.01	0.00	871	437	8.87	60.1	50	41.4	2.9	360
49.6	84.1	50.09	50.09							
	12	0.01	0.00	1208	644	8.42	63.2	43	40.1	3.6	66
44.4	84.3	42.59	42.59							
	13	0.01	0.00	962	500	7.73	63.8	38	37.9	4.1	92
37.0	84.6	38.26	38.26							
	14	0.01	0.00	633	281	7.71	63.6	38	37.8	4.8	89
21.5	84.9	38.36	38.36							
	15	0.01	0.00	653	296	7.66	64.2	37	37.7	4.0	91
24.8	85.2	37.41	37.41							
	16	0.01	0.00	479	186	7.67	64.1	38	37.7	3.4	83
27.7	85.5	37.54	37.54							
	17	0.00	0.00	71	-29	7.89	61.4	42	38.4	2.4	77
14.3	85.7	42.52	42.52							
	18	0.00	0.00	1	-39	8.11	57.6	50	39.1	1.2	81
54.6	85.9	50.01	50.01							
	19	0.00	0.00	0	-38	9.32	54.5	64	42.7	1.4	215
44.3	85.9	64.40	64.40							
	20	0.00	0.00	0	-37	9.71	53.4	70	43.8	1.1	266
27.8	85.9	69.86	69.86							
	21	0.00	0.00	0	-37	9.60	52.4	71	43.5	1.4	343
52.2	85.9	71.50	71.50							
	22	0.00	0.00	-1	-38	8.96	52.6	66	41.7	1.0	71
25.0	85.8	66.25	66.25							
	23	0.00	0.00	-1	-37	9.52	51.7	73	43.3	1.8	200
34.1	85.7	72.80	72.80							
	24	0.00	0.00	0	-36	9.76	51.0	76	43.9	1.8	241
19.9	85.6	76.50	76.50							
1/22/95	0.07	= TOTAL ETo								

calorie/sq.cm/day (Ly/day)*.484=W/sq.m inches*25.4=mm (F-32)*5/9=C

mph*.447=m/s mBars*.1=kPa

---------- SEVERE FLAGS ----------

FORMATIVE FLAGS ----------

M/C -not collected N/A -not available noc -cannot calculate Y -out of range

-all quality control not performed

S -not in service R -out of range I -ignore,no meaning F -estimated

note: TOTAL ETo = s

* * * *

APPENDIX V

1992 BROMOXYNIL APPLICATION REPORT

State of California

AIR RESOURCES BOARD

BROMOXYNIL APPLICATION MONITORING REPORT

Ambient Air Monitoring in Imperial County for Bromoxynil in January, 1992, after Application to a Wheat Field

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C87-117A

Report Date: June 29, 1992

APPROVED:

_____, Project Engineer
Testing Section

_____ Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

Bromoxynil Monitoring in Imperial County in January, 1992

This report presents the results of ambient monitoring for bromoxynil after an aerial application at a selected wheat field in Imperial County. The results are based on samples collected and analyzed by the Air Resources Board Monitoring and Laboratory Division staff. The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

Kevin Mongar assisted in the collection of samples. Gerald Edwards of Stoker Co. greatly assisted in arranging for a suitable field to monitor. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses were performed by the Northern Laboratory Branch of the ARB.

APPENDIX VI
QMOSB AUDIT REPORT

STATE OF CALIFORNIA

AIR RESOURCES BOARD

AUDIT REPORT

BROMOXYNIL MONITORING IN IMPERIAL COUNTY

MONITORING AND LABORATORY DIVISION

QUALITY ASSURANCE SECTION

APRIL 18, 1995

AUDIT REPORT

BROMOXYNIL MONITORING IN IMPERIAL COUNTY

TABLE OF CONTENTS

ATTACHMENTS

LIST OF FIGURES

I. EXECUTIVE SUMMARY

In January of 1995, the Engineering and Laboratory Branch of the California Air Resources Board conducted ambient air sampling in Imperial County, California, to document the airborne emissions of bromoxynil in the vicinity of a treated field during and after an application. The samples were analyzed by the Engineering and Laboratory Branch.

The Monitoring and Laboratory Division's Quality Assurance Section staff conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (California Air Resources Board, February 4, 1994).

Additionally, Quality Assurance Section staff conducted performance audits of the air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The difference between the reported and true flow rates averaged 0.23% with a range of -1.08% to 2.79%. In order to determine the effectiveness of the analytical procedure, laboratory performance audits were also conducted. On January 27, 1995, seven samples spiked with measured amounts of bromoxynil were submitted to the laboratory for analysis. The samples were prepared from a bromoxynil standard solution obtained from Chem Service. The difference between the assigned and the reported total mass averaged -58.5% with a range of -80.8% to -49.3%. When the results were returned to the Quality Assurance Section, an investigation was initiated to determine the cause of the excessive percent differences. It was found that the audit samples had been partially extracted on January 27, 1995, and then capped and stored in the refrigerator over the weekend. On Monday, January 30, 1995, the extraction process was resumed and the samples were analyzed. Field samples were fully extracted and analyzed in one day. Therefore, it was determined that the two day storage of the partially extracted audit samples contributed to the low recovery.

On February 2, 1995, a second laboratory performance audit was conducted. A set of five audit samples spiked with measured amounts of bromoxynil were submitted to the laboratory for analysis. These samples were prepared from the same bromoxynil standard solution as the first set of audit samples. The difference between the assigned and the reported total mass averaged 12.2% with a range of -6.4% to 32.0%.

II. CONCLUSIONS

The records for field operations, sample handling procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring. The results of the reported flow rates were in good agreement with the actual flow rates measured by Quality Assurance Section staff. The results of the second analytical performance audit showed an average of 12.2%. Based on these results, it was determined that the results of the first analytical performance audit were unreliable due to the two day storage of the partially extracted samples.

Stability studies have been conducted for a maximum period of seven days at -4 degrees celsius (^{o}C). Samples were stored in the field for four to seven days before being shipped to the laboratory. The samples were received by the laboratory on January 25, 1995 and extracted on January 27, 1995 and analyzed three days later. Therefore, the samples that had been stored in the field for seven days had already exceeded the maximum time period determined by the stability studies before they were extracted and analyzed in the laboratory. However, the high level of recovery of the field spikes, 96%, indicates that the delays in analysis of the samples did not adversely impact the validity of the data.

This laboratory performance audit was the first to use a standard spiking solution purchased from the vendor. In the past, a negative bias has been observed in the audit results, which was thought to be due to dilution error during the preparation of the audit samples. It appears that purchase of a standard solution of the audit material from the vendor has eliminated the negative bias that has been observed in past audits. Quality Assurance Section staff will continue to purchase standard solution audit materials and to evaluate the effectiveness of these solutions based upon audit results.

III. RECOMMENDATIONS

The laboratory audit procedure is designed to provide feedback on the reliability of field sample data and on the procedure used to analyze the field samples. Therefore, audit samples should always be handled and analyzed in a manner consistent with the handling and analysis of field samples.

Stability studies should be conducted for a time period equal to or longer than the longest anticipated sample storage time prior to analysis.

IV. INTRODUCTION

In January of 1995, the Engineering and Laboratory Branch (ELB) of the California Air Resources Board (CARB) conducted ambient air sampling in Imperial County, California, to document the airborne emissions of bromoxynil in the vicinity of a treated field during and after an application. The samples were analyzed by the ELB. Monitoring and Laboratory Division (MLD) Quality Assurance Section (QAS) staff conducted a system audit of the field and laboratory operations, and performance audits of the air samplers and the analytical method.

V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices for the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (CARB, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rate and the analytical method.

VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in January 1995 through a questionnaire submitted to ELB staff. Additionally, the protocol for ambient air monitoring of bromoxynil and the laboratory's standard operating procedure for the analysis of bromoxynil were reviewed. The following is a discussion of the audit findings.

Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through glass tubes containing 600 mg of XAD-2 adsorbent resin. The air samplers consisted of two sampling tubes, each connected with Teflon tubing to an in-line rotameter, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Figure 1). The samplers' rotameters were set to an indicated flow rate of 2.0 liters per minute (LPM) by adjusting the control valve on the rotameter.

Sampling was conducted following the schedule specified in the sampling protocol. After sampling, the exposed XAD-2 tubes were collected, capped, and placed in screw-cap glass culture tubes. The tubes were then stored over ice in an ice chest until they were delivered to the laboratory at the end of the three day sampling period.

Samples were stored in the field for four to seven days before being shipped to the laboratory. The samples were extracted two days after being received at the laboratory, and analyzed three days later. According to the stability study, the integrity of bromoxynil is verified for seven days when stored at -4 °C. Therefore, the field samples that had been stored for seven days before being submitted to the laboratory were extracted and analyzed after the maximum time period for the stability studies had elapsed.

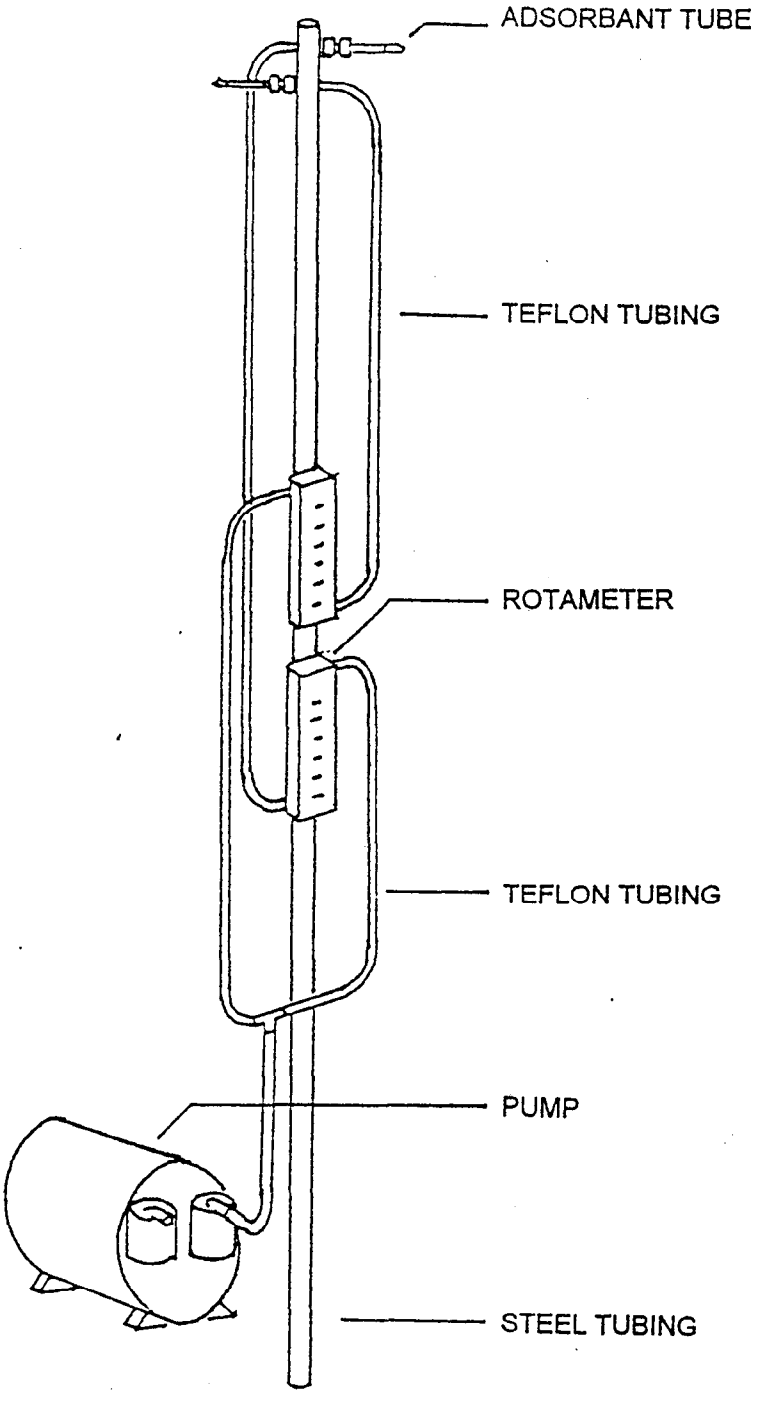

Figure 1. Air sampler used in the monitoring of bromoxynil

Sample Analysis

The analytical method used was a modified version of the United States Environmental Protection Agency's Method 1661 "The Determination of Bromoxynil in Municipal and Industrial Wastewater". The method calls for extraction of the sampling tubes with acetone. The acetone is evaporated and replaced with water followed by 70/30 water/methanol isocratic reverse phase high performance liquid chromatography (HPLC). The analyses were performed with a Waters HPLC.

The chromatograph was calibrated before each analytical run. Calibration standards of 0.100, 0.600, and 3.000 ug/ml were prepared just before analyses from a neat bromoxynil sample obtained from Chem Service. The standards were stored in a freezer, and were determined to be stable for one month.

Quality control activities performed to monitor and document the quality of the data included analysis of a laboratory spike and field spikes; analysis of a method blank; one field blank per shipment of samples; and analysis nine collocated samples. One control sample was run for every 10 field samples.

Method Validation

The limit of detection (LOD) was defined as three times the standard deviation of five readings. The LOD was calculated as 0.045 ug per sample. Trapping efficiency was determined as 73%. Stability studies were conducted for samples stored at -4 ^{o}C. After seven days, the recovery was 94%.

Documentation

All the samples received at the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were retained by ELB staff. The information recorded in the field data sheets included sampler location, sampling date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date sample was received, date of analysis, results of analysis, and analyst.

The raw analytical data were stored in electronic files, and hard copies of the run data and chromatograms will be kept for five years.

VII. PERFORMANCE AUDITS

Flow Rate Audit

The flow rate of each sampler used for the monitoring was audited on December 16, 1994, following the procedures outlined in Attachment I. The audit was conducted with a 0 to 3 LPM mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the reported and true flow rates averaged 0.23% and ranged from -1.08% to 2.79% (Table 1).

Table 1. Results of the flow rate audit of the samplers used in the monitoring of bromoxynil.

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1A	1.84	1.85	-0.54
1B	1.84	1.84	0.00
2A	1.84	1.86	-1.08
2B	1.84	1.85	-0.54
3A	1.84	1.84	0.00
3B	1.84	1.86	-1.08
4A	1.84	1.83	0.55
4B	1.84	1.80	2.22
5A	1.84	1.84	0.00
5B	1.84	1.79	2.79

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

Laboratory Performance Audit

The accuracy of the analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with measured amounts of bromoxynil. The samples were prepared by QAS staff on January 27, 1995, following the procedures outlined in Attachment II, and they were partially extracted on the same day. On January 30, 1995, extraction was completed and the samples were analyzed. The difference between the assigned and the reported total mass of bromoxynil averaged -58.5% with a range of -80.8% to -49.3% (Table 2). Quality Assurance Section and ELB staff conducted an investigation to determine the reason for the large percent difference and concluded that the low recovery was due to the two day period between the start and the completion of the extraction process.

Table 2. Results of analyses of the bromoxynil audit samples (first set).

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
BRX-1	0.50	0.249	-50.2
BRX-2	0.00	<0.02	0.0
BRX-3	1.00	0.507	-49.3
BRX-4	0.50	0.211	-57.8
BRX-5	0.25	0.048	-80.8
BRX-6	1.00	0.421	-57.9
BRX-7	0.25	0.112	-55.2

A second set of audit samples was prepared by QAS staff and submitted to the laboratory on February 2, 1995. These samples were prepared using the same bromoxynil spiking solution and following the same procedure as the first set of audit samples. The samples were extracted and submitted for analysis on February 2, 1995. The difference between the assigned and reported total mass of bromoxynil averaged 12.2% with a range of -6.4% to 32.0% (Table 3). The results of the second audit set were much more consistent with the expected recovery. It is likely that the percent difference values for samples BRX-9 and BRX-11 were higher than the others because these sample volumes were 5 ul, which is at the low end of the confidence area for our microsyringe.

Table 3. Results of analyses of the bromoxynil audit samples (second set).

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
BRX-8	0.375	0.381	1.6
BRX-9	0.125	0.165	32.0
BRX-10	0.750	0.702	-6.4
BRX-11	0.125	0.165	32.0
BRX-12	0.375	0.381	1.6

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

ATTACHMENT I

Flow Rate Audit Procedures for Air Samplers
Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST-traceable flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.

2. Calibrated differential pressure gauge with laminar flow element.

3. 1/4" O.D. Teflon tubing.

4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.

2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.

3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.

4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.

5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

ATTACHMENT II

Performance Audit Procedures
for the Laboratory Analysis of Bromoxynil

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory to measure the ambient concentrations of bromoxynil. The audit is conducted by submitting audit samples spiked with known concentrations of bromoxynil. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Bromoxynil - neat, 99% pure, Chem Service, Lot # 126-107A, was used to make the following spiking solution: Bromoxynil at 0.025 ug/uL in methanol, Chem Service, Lot # 150-4C

2. XAD-2 adsorbent tubes, 600 mg, SKC, Lot# 816

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Preparation of Audit Samples

Prepare seven audit samples by spiking XAD-2 adsorbent tubes with the volume of bromoxynil spiking solution indicated in the table below. Using a microsyringe, insert the needle into the primary section of the XAD-2 tube, and push the plunger slowly while rotating the tube. Avoid contact of the spiking solution with the tube walls.

Sample ID	Bromoxynil Spiking Solution Volume (ul)
BRX-1	20
BRX-2	0
BRX-3	40
BRX-4	20
BRX-5	10
BRX-6	40
BRX-7	10

Prepare five audit samples following the procedure indicated above.

Sample ID	Bromoxynil Spiking Solution Volume (ul)
BRX-8	15
BRX-9	5
BRX-10	30
BRX-11	5
BRX-12	15

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State of California
Air Resources Board

Bromoxynil Monitoring in Imperial County

I. INTRODUCTION

At the request of the California Department of Pesticide Regulations (DPR), formerly the Department of Food and Agriculture, and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a three-day source impacted ambient monitoring program for bromoxynil in Imperial County during the month of January, 1992.

The ambient monitoring for bromoxynil occurred during January, 1988. Because of weather conditions and time constraints, the application monitoring was postponed until this year.

II. PESTICIDE DESCRIPTION

Bromoxynil (molecular weight 276.92 g/mole) is a selective herbicide which is a white, odorless solid with a melting point of 194-195°C. It has a vapor pressure of less than 10^{-5} mm Hg at 20°C. It is only slightly soluble in water (0.13 gm/l), but is soluble in acetone (170 gm/l) and tetrahydrofuran (410 gm/l).

While bromoxynil is not regulated as a restricted use material under section 6400, Title 3 of the California Administrative Code, it is a Category II pesticide and subject to the provisions of the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65).

III. SAMPLING LOCATIONS

A wheat field of about 75 acres was selected (FIGURE I.) by Gerald Edwards of Stoker Co. and approved by ARB staff to use for application monitoring. The prevailing wind in the area is from the northwest. Three samplers were set up: 1) approximately 15 yards northwest of the field, 2) approximately 15 yards southeast of the field and 3) approximately one quarter mile southeast of the field. A meteorological station was set up near the downwind sampler (SE1) nearest the field (FIGURE II.)

The application was by airplane and took about forty-five minutes. The application rate was one and one-third pints Buctril (bromoxynil) per acre.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through XAD-2 tubes (see APPENDIX I.) These tubes are 8mm x 110mm, with 400 mg in the primary section and 200 mg in the secondary (SKC catalog #226-30-06). Any bromoxynil present in the sampled ambient air is captured by the XAD-2 adsorbent contained in the tubes. Subsequent to sampling, the tubes were transported in an iced container to the ARB Monitoring and Laboratory Division laboratory in Sacramento for analysis.

Sampling trains designed to operate continuously were set up at the three sampling sites identified in FIGURE II. Duplicate samples were obtained from all three sites. Sampling tubes were changed, as closely as practical, according to the schedule outlined in the QA Plan for Pesticide Monitoring (APPENDIX II.)

Each sample train consisted of an XAD-2 tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a 12VDC battery-powered vacuum pump. A diagram of the sampling train is shown in FIGURE III. Each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. Covers were wrapped around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration prior to use in the field indicated that an average flow rate of 1.86 lpm was actually achieved when the rotometers were set to 2.0 lpm.

At the end of each sampling period the final indicated flow rate (if different than the set 2.0 lpm), the stop date and time were recorded. The XAD-2 tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest until the tubes were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The XAD-2 tubes recovered from each sampler were analyzed by the NLB staff. The XAD-2 in the primary section of each sample tube was extracted with ammoniacal methanol, converted to the methyl ester followed by GC separation on a DB-1 or DB-5 capillary column and measurement by Electron Capture Detector (APPENDIX III.) The secondary (backup) sections were saved to check for breakthrough, if necessary.

VI. RESULTS

As discussed in "Sampling Locations", the samplers were set up based on the prevailing wind coming from the northwest. As can be seen from TABLE II., the wind seemed to be quite variable during the sampling period. Unless there is a strong indication otherwise, samplers are always set up based on historical prevailing winds regardless of the direction at the actual time of set up.

Results for bromoxynil are shown in TABLE I. and APPENDIX IV. A summary of the results along with meteorological data is shown in TABLE II. As TABLE I. shows, very low levels of bromoxynil were found. The highest level was for sample 2SE1, 2.07 ug/m^3 (average of duplicates), with the remaining values all below one ug/m^3. The duplicate samples also show good correlation.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the S.O.P. for bromoxynil (APPENDIX IV.)

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX III.) were followed. Spikes were prepared by the Quality Management and Operations Support Branch of the ARB. The complete QA audit report is in APPENDIX V., including data for the flow rate audit. A summary of the laboratory audit (spikes) results are shown in TABLE III. The difference between the assigned and the reported values ranged from -39 to +20%.

TABLE I. BROMOXYNIL MONITORING DATA

Sample ID	Sample Time (min.)	Sample Flow (lpm)	Sample Volume m^3	Amount Detected ug	Concentration ug/m^3
0NW	85	1.86	0.158	<0.02	—
0NW	85	1.86	0.158	<0.02	—
0SE1	95	1.86	0.177	<0.02	—
0SE1	95	1.86	0.177	<0.02	—
0SE2	100	1.86	0.186	<0.02	—
0SE2	100	1.86	0.186	<0.02	—
1NW	120	1.86	0.223	0.18	0.81
1NW	120	1.86	0.223	0.22	0.99
1SE1	135	1.86	0.251	<0.02	—
1SE1	135	1.86	0.251	0.04	0.16
1SE2	135	1.86	0.251	<0.02	—
1SE2	135	1.86	0.251	<0.02	—
2NW	110	1.86	0.205	<0.02	—
2NW	110	1.86	0.205	0.05	0.24
2SE1	110	1.86	0.205	0.48	2.34
2SE1	110	1.86	0.205	0.37	1.80
2SE2	110	1.86	0.205	<0.02	—
2SE2	110	1.86	0.205	<0.02	—
3NW	310	1.86	0.577	0.19	0.33
3NW	310	1.86	0.577	0.33	0.57
3SE1	310	1.86	0.577	0.22	0.38
3SE1	310	1.86	0.577	0.24	0.42
3SE2	315	1.86	0.586	<0.02	—
3SE2	315	1.86	0.586	<0.02	—
4NW	720	1.86	1.339	0.41	0.31
4NW	720	1.86	1.339	0.42	0.31
4SE1	720	1.77	1.274	0.23	0.18
4SE1	720	1.77	1.274	0.30	0.24
4SE2	715	1.86	1.330	0.18	0.14
4SE2	715	1.86	1.330	0.12	0.09
5B	BLANK	—	—	<0.02	—
5NW	1375	1.86	2.558	0.04	0.02
5NW	1375	1.86	2.558	0.06	0.02
5SE1	1375	1.67	2.296	0.05	0.02
5SE1	1375	1.67	2.296	0.08	0.03
5SE2	1385	1.86	2.576	0.09	0.03
5SE2	1385	1.86	2.576	<0.02	—
6NW	1390	1.86	2.585	<0.02	—
6NW	1390	1.86	2.585	<0.02	—
6SE1	1390	1.86	2.585	<0.02	—
6SE1	1390	1.86	2.585	<0.02	—
6SE2	1385	1.86	2.576	<0.02	—
6SE2	1385	1.86	2.576	<0.02	—

TABLE II. SUMMARY OF BROMOXYNIL DATA

Concentration (ug/m^3)

Sampling Period	Site "NW"	wind	Site "SE1"	Site "SE2"	
0	ND	 W/S 4 mph	ND	ND	(Background)
1	0.90	 W/S 2 mph	0.08	ND	(Application)
2	0.12	 W/SW 2 mph	2.07	ND	
3	0.45	 NE/NW 3 mph	0.40	ND	
4	0.31	 E/SE 2 mph	0.21	0.12	
5	0.02	 SE/E/S 4 mph	0.02	0.02	
6	ND	 NE/E 3 mph	ND	ND	

ND indicates not detected, <0.02 ug/sample.
Arrowhead indicates direction wind is blowing toward.
BOLD indicates predominate wind direction, if any.

TABLE III. BROMOXYNIL QUALITY ASSURANCE DATA

Sample ID	Assigned Value	Reported Value	% of Assigned Value
B-1	1.99 ug	1.81 ug	90
B-2	0.50 ug	0.60 ug	120
B-3	0.00 ug	<0.02 ug	N/A
B-4	1.99 ug	1.80 ug	90
B-5	1.00 ug	0.95 ug	95
B-6	3.98 ug	3.00 ug	75
B-7	1.00 ug	0.61 ug	61

FIGURE I. PESTICIDE MONITORING AREA

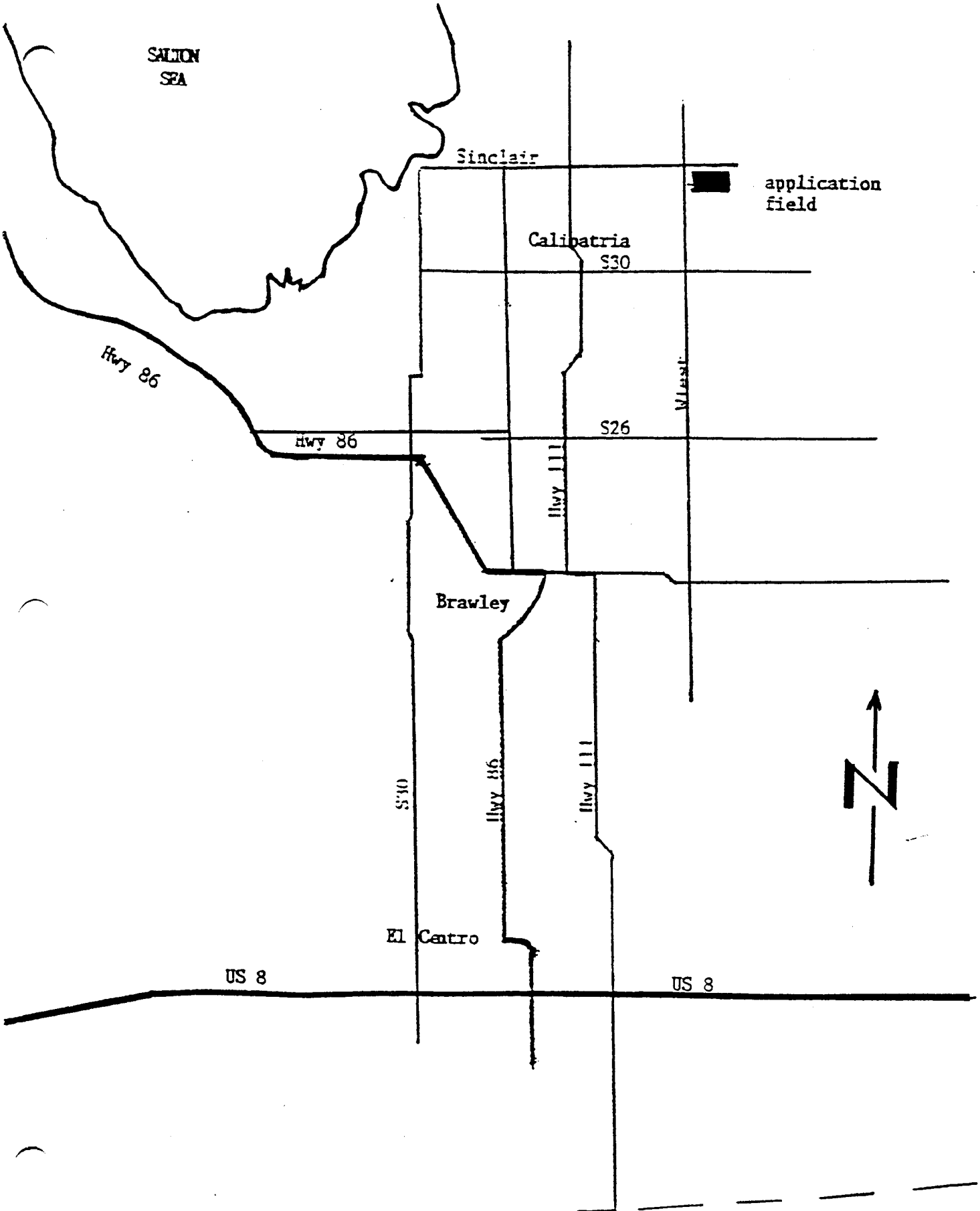


FIGURE II. PESTICIDE MONITORING SITES

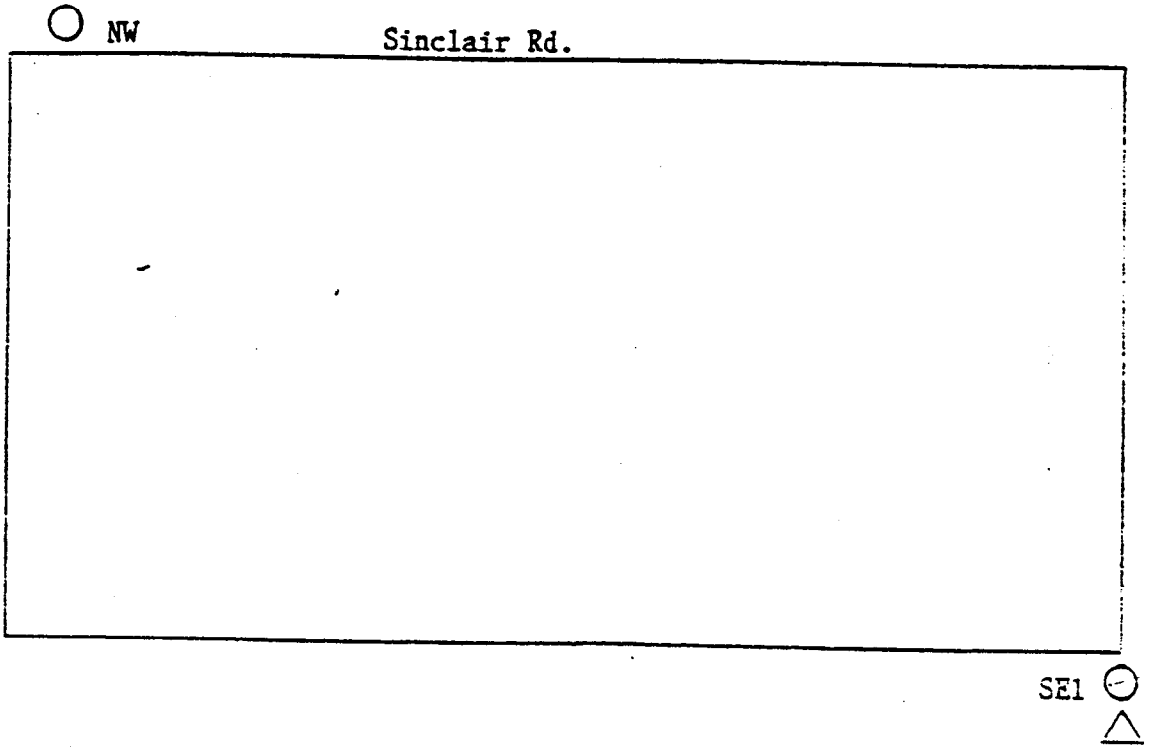
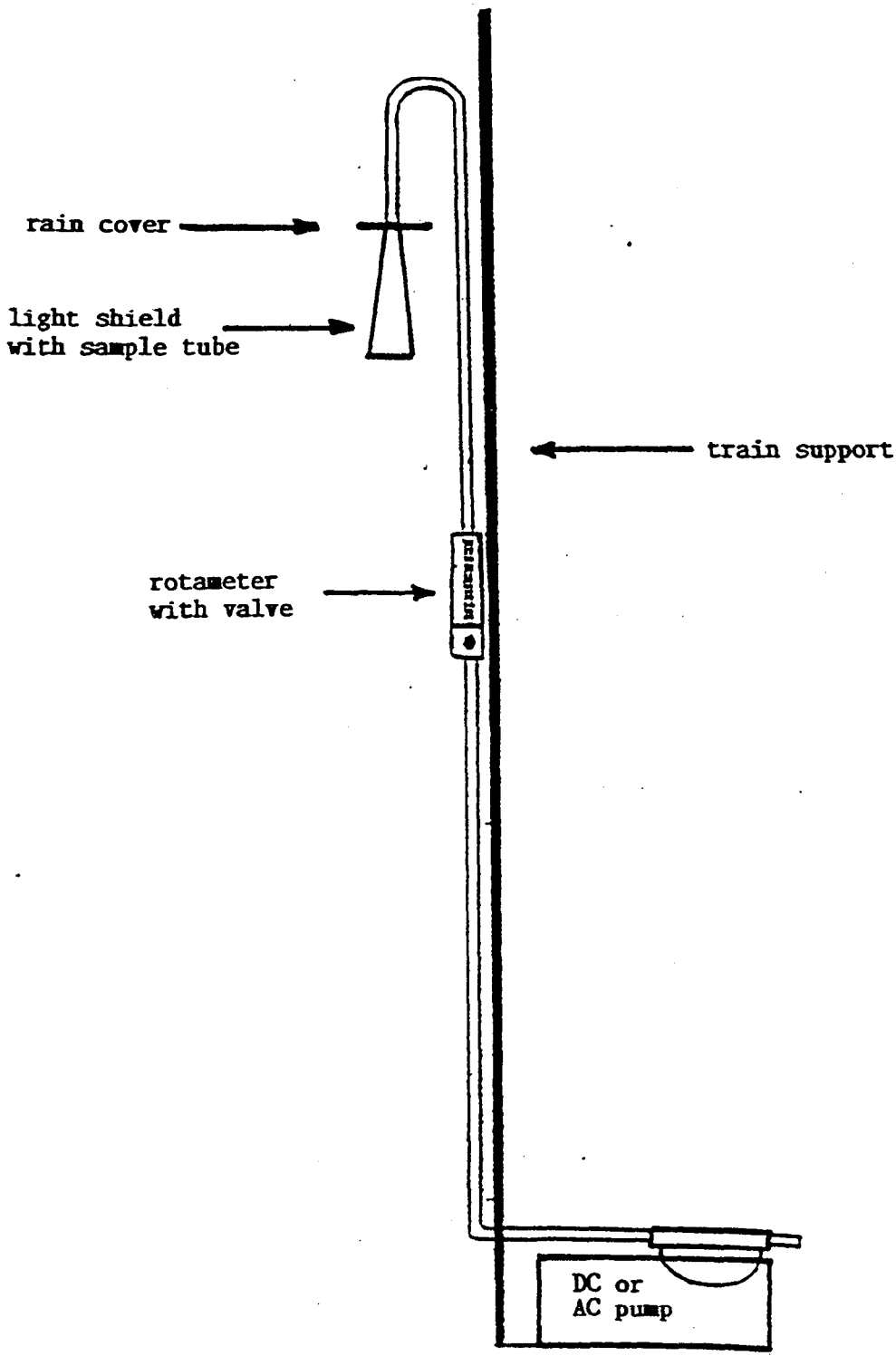


FIGURE III. PESTICIDE MONITORING APPARATUS



CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: ___/___/___
Sample/Run #: _____ Time: _____
Job name: _____
Sample Location: _____
Type of Sample: _____
Log #'s: _____

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: _____

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX I.

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

Bromoxynil Application Monitoring in Imperial County

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C87-117A

Report Date: January 16, 1992

APPROVED:

_____, Project Engineer
Testing Section

_____, Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

January 16, 1992

Protocol for Bromoxynil Application Monitoring in Imperial County

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) will conduct a 3-day source impacted ambient monitoring program for bromoxynil in Imperial County. Bromoxynil is a selective herbicide used on a wide variety of crops. Peak use in California is for wheat in Imperial County during the winter months.

II. Sampling

Prior to application, background samples will be taken to establish if any bromoxynil is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with XAD-2 tubes using battery powered pumps capable of flows of approximately 2 liters per minute. Three samplers will be used; 1) one 15 yards upwind of the field, 2) one 15 yards downwind and 3) one 150 yards downwind. These distances are approximate and dependent on the physical obstacles surrounding the field. As closely as feasible, the sample tubes will be changed according to the schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring".

Calibrated rotometers will be used to control sample flow rates. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. Any change in the flow rates will be recorded in a log book, along with any other pertinent information.

III. Analysis

All samples will be stored in an ice chest or refrigerator until analysis. Analysis of samples will be by gas chromatography using and electron capture detector (ECD). The analytical procedure is fully described in ARB's "Method for the Determination of Bromoxynil and Bromoxynil Esters in Ambient Air" (NLB 026).

IV. Quality Assurance

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. Sample flow rates will be calibrated prior to and after sampling in the field.

A chain of custody sheet will accompany all samples. A field log book will be used to record start and stop times, sample ID's and any other significant data.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers (Instrument Technician).

APPENDIX II.

State of California
Air Resources Board

Quality Assurance Plan for Pesticide Monitoring

Prepared by the

Monitoring and Laboratory Division
and
Stationary Source Division

September 28, 1990

APPROVED:

Geroniare A Shuma, Chief,
Toxic Air Contaminant
Identification Branch
Stationary Source Division

_____, Chief,
Quality Management and
Operations Support Branch
Monitoring and Laboratory Division

George Lew, Chief,
Engineering Evaluation Branch
Monitoring and Laboratory Division

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Food and Agriculture (DFA), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. Short-term (one month) ambient monitoring will be conducted in the area of, and during the season of, peak pesticide applications. In addition, monitoring of a field during and after application (up to 72 hours) will occur. The purpose of this document is to specify quality assurance activities for sampling and laboratory analysis of the pesticide.

II. Quality Assurance Policy Statement

It is the policy of the ARB to provide DFA with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

III. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: 1) to establish the necessary quality control activities relating to site selection, sample collection, sample analysis, and data validation, and 2) assessment of data quality in terms of precision, accuracy and completeness.

IV. Siting

Siting criteria for ambient pesticide monitoring are listed in TABLE 1. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. Background sites should be located away from any applications.

Siting criteria for placement of samplers near a pesticide application for collection of short-term samples are: 1) fifteen yards upwind of the field, 2) fifteen yards downwind of the field, and 3) 150 yards downwind of the field. These are only guidelines, since conditions at the site will dictate the placement of monitoring stations. Data on wind speed and direction will be collected during application monitoring. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed. Field application monitoring will follow the schedule outlined in TABLE 2. This schedule and study design are consistent with requests from DFA for monitoring near a pesticide application.

A. Monitoring Site Description

The protocol for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions).

Similarly, a map or sketch of the monitoring stations should be made with respect to the application field.

V. Sampling

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Sampling will be conducted following the Environmental Protection Agency (EPA) ambient monitoring guidelines of 40 CFR 58 for calibration, precision, accuracy and data validation. The ARB Quality Assurance Section upon request will review quality assurance/quality control procedures and will evaluate pesticide monitoring activities.

A. Protocol

Prior to conducting any pesticide monitoring a protocol will be written that describes the overall monitoring program and includes the following topics:

1. Identification of the sample site locations.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.)

3. Description of the analytical method.

4. Quality assurance/quality control plan for sampling, including calibration procedures for flow meters.

5. Test schedule.

6. Test personnel.

Specific sampling methods and activities will be described in a monitoring plan (protocol) for review by ARB and DFA. Criteria which apply to all sampling are: 1) chain of custody forms will accompany all samples (APPENDIX I.), 2) light and rain shielding will be used for samples during monitoring and, 3) samples will be stored in an ice chest until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to this specific pesticide.

B. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample type (e.g., charcoal tube), sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Field blanks should be included with each batch of samples submitted to the lab for analysis. The average of the initial and final flow rates for the sampling period will be used if a flow controller is not used.

C. Collocation

For ambient monitoring, sampling precision or the standard deviation of the data set will be calculated from at least 2 samples collocated at a site. The collocated sampler will be rotated between sampling sites so that at least three duplicate samples are collected at each site. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. One sample will be designated as the primary sample and the other sample will be designated as the duplicate.

D. Calibration

If elapsed time meters are used, rather than noting beginning and ending times, the meters should be checked and calibrated to within $\pm$ 5 minutes for a 24-hour period. Samplers operated with an automatic on/off timer should be calibrated so that the sampling period is 24 hours $\pm$ 15 minutes.

Flow meters, flow controllers or critical orifices should be calibrated against a referenced flow meter prior to a monitoring period.

Sampling flows should be checked in the field and noted before and after each sampling period. Before flows are checked, the sampling system should be leak checked. The initial flow should be within $\pm$ 10% if a calibrated pressure transducer is used to check the flows, or within $\pm$ 15% if a calibrated rotameter is used. Flow meters should be recalibrated if flows are found to be outside of those control limits.

E. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc. should be made by sampling personnel.

TABLE 1. PESTICIDE MONITOR SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. APPLICATION SAMPLING SCHEDULE

The sampling schedule for each station is as follows:

	Samples per Site*		
	~15 yds up-wind	~15 yds down-wind	~150 yds down-wind
- Background sample (1 hr. sample: prior to application).	2	2	2
- Application + 1 hr. after application combined sample.	2	2	2
- 2 hr. sample from 1 to 3 hours after the application.	2	2	2
- 4 hr. sample from 3 to 7 hours after the application.	2	2	2
- 8 + hr. sample from 7 to 15+ hours after the application.	2	2	2
- 9 + hr. sample from 15 to 24+ hours after the application.	2	2	2
- 1st 24 hour sample starting at the end of the 9+ hr. sample.	2	2	-
- 2nd 24 hour sample starting 24 hrs after the end of the 9+ hr. sample.	2	2	-

* duplicate collocated samples at each site.

VI. Analysis

Analytical audits should be conducted by spiking the sample medium with the reference standard. These can then be carried into the field and handled as actual samples (trip spike) or run at the background site for ambient monitoring (field spike) prior to delivery to the laboratory for analysis. At least one spike per monitoring period is required and one spike per week is recommended for ambient monitoring.

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. should include: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures.

A. Standard Operating Procedures

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The monitoring plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable gas standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Assurance

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as; use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of lab analysis and after every tenth sample. Control samples should be found to be within control

limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked tubes at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VII. Data Reduction and Reporting

The mass of pesticide (microgram, ug) found in each sample will be used along with the sample air volume from the field data sheet to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in ug/m^3 as well as ppb or ppt (as appropriate). Wind speed and direction data will also be reported for application site monitoring.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum detection limit), total number of samples and number of samples above the minimum detection limit. For this purpose, collocated samples are averaged and treated as a single sample.

A. Quality Assurance

Quality assurance activities and data will be summarized by the staff conducting the sampling and included as an attachment to the final data summary. The quality assurance report will include a summary of the average data precision, accuracy, and completeness.

1. Precision and Accuracy

The average precision or standard deviation will be reported based on the comparison of the collocated sampling data. Accuracy data to be reported includes the results of the analyses of spiked samples and the results of any flow audits.

2. Data Completeness

Data completeness should be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred. Data will be invalidated if the power is out at a site and the length of a sample time cannot be verified, or if any of the sampling medium is lost during sampling, shipment or analysis.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: / /
Sample/Run #: _____ Time: _____
Job name: _____
Sample Location: _____
Type of Sample: _____
Log #: _____

ACTION	DATE	TIME	INITALS	
Sample Collected				
			GIVEN BY	TAKEN BY
Transfer				
Transfer				
Transfer for Analysis				

ID #	LOG #	DESCRIPTION

RETURN THIS FORM TO: _____

APPENDIX III.

CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

S.O.P. No. MLD 026

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF BROMOXYNIL AND BROMOXYNIL ESTERS IN AMBIENT AIR

1. SCOPE

This document describes a method for the sampling and analysis of bromoxynil (2,4-dibromo-hydroxybenzonitrile) and bromoxynil esters at concentrations normally expected in ambient air. The method was developed from the work of Crouch and Pullin (Pestic. Sci., 5, pg 281, 1974).

2. SUMMARY OF METHOD

After sampling using a low-volume system comprising a sample pump, calibrated flow controller, and purified XAD-2 sorbent trap, the exposed XAD-2 resin is desorbed with 2.0 ml. ammonical methanol, acidified, and back extracted with toluene. The phenol is then reacted with diazomethane to form the methyl ether derivative. Two microliters are injected into a gas chromatographic system equipped with a splitless injector, DB-1 capillary column, and electron capture detector. The resultant peak is identified by a characteristic retention time and quantitated in reference to external standards.

3. INTERFERENCES/LIMITATIONS

Components having similar GC retention times will interfere, causing misidentification and/or erroneous quantitation. Positive results are confirmed using a DB-1301 capillary column.

4. APPARATUS

4.1 Perkin-Elmer Model 8500 Gas Chromatograph/ECD/Data System.

4.2 DB-1 fused silica capillary column, 30 meters X 0.35 mm i.d., 0.25 micron film thickness.

4.3 Amber vials, 3.7 ml capacity, with teflon-lined septum caps.

4.4 Sample agitator with timer.

4.5 XAD-2 glass absorption tubes, containing 400 mg in primary section, 200 mg in secondary section.

4.6 Millimolar diazomethane generator, Pierce #28131, or equiv.

5. REAGENTS

5.1 Ammonical Methanol: Mix 10 ml. concentrated ammonium hydroxide with 190 ml methanol. Store in amber glass container.

5.2 Toluene, Pesticide Grade, or equivalent.

5.3 Diazomethane Reagent: CAUTION: DIAZOMETHANE IS EXTREMELY TOXIC AND CAN EXPLODE AT HIGH TEMPERATURES OR IF SUBJECTED TO SHOCK. AVOID GROUND GLASS JOINTS. USE EXTREME CAUTION AND WEAR GLOVES. PREPARE IN FUME HOOD.

Place 100 mg of N-methyl-N-nitroso-N'-nitroguanidine into the inside tube of the millimolar generator. Add 0.5 ml water. Place 3 ml diethyl ether in the outside tube and assembly the generator. Insert the lower part of the generator into an ice bath. Using a 1 ml syringe, inject 0.6 ml of 5N sodium hydroxide through the septum into the inside tube. INJECT THE SODIUM HYDROXIDE SOLUTION SLOWLY, AS THERE WILL BE A PRESSURE BUILD-UP. Let the generated diazomethane accumulate in the cold ether for 45 minutes. Carefully disassemble the apparatus and transfer the ether/diazomethane solution to a 5 ml amber glass screw-capped vial with teflon septum. Keep refrigerated. This reagent is good for one week.

5.3 Stock Standard: 1000 ug/ml: Dissolve 0.100 gram bromoxynil (Chem Service, 99+%) in 100 ml Pesticide Grade toluene.

5.4 Calibration Standard: 1.0 ug/ml: dilute 100 ul of Stock Standard to 100 ml with toluene.

6. INSTRUMENT CONDITIONS

Column: 30m X 0.35 mm i.d. DB-1 fused silica capillary column

Temperature: Injector: 300 C
Detector: 350 C
Oven: 60 C initial, hold for 1 min; ramp ballistically to 140 C, hold for 1 min; ramp at 5 C/min to 260 C, hold for 5 min.

Detector: ECD

Flow Rates: Carrier: He at 25 cm/sec; 30 cc/min at splitter, 0.7 min. splitless hold. 60 cc/min Nitrogen detector make-up gas.

7. ANALYSIS PROCEDURE

7.1 Calibration standards and solvent blanks must be analyzed in the same manner as samples. The calibration standards, 1.0 ug/ml and 0.1 ug/ml in toluene, are derivatized with diazomethane along with each batch of samples analyzed.

7.2 After removal of the red end caps of the XAD-2 tubes, the tube is scored with a glass cutter above the location of the retainer spring. The glass wool plug and the primary section (400 mg) is placed in a 3.7 ml amber glass vial. The secondary section is retained for later analysis if the results of the primary section are positive. Make sure that all vials are properly identified.

7.3 Place 2.0 ml of the ammonical methanol solution in the vials and place on agitator for 90 minutes. Remove 1.0 ml of the extract and place in a 15 ml screw-capped centrifuge tube. Allow to stand for 2 hrs.

7.4 Add 1 ml of aqueous 6N hydrochloric acid, mix, and add 4.0 ml of Pesticide Grade toluene. Shake for one minute and allow the phases to separate. Repeat the extraction. Remove 2.0 ml of the toluene extract and place in an amber screw-capped glass vial.

7.5 Add 100 ul of the diazomethane/ether solution to toluene extracts, calibration standards, and solvent blank. Mix and allow to stand overnight.

7.6 Inject 2.0 ul of the standards, blanks, and sample extracts into the gas chromatographic system using Grob splitless technique. Compare the results of the analysis of the calibration standards to previous analyses to insure consistent response. The total mass of bromoxynil per sample is calculated as follows:

$$\text{ug/sample} = \frac{\text{Stnd Conc. X Sample Area Count X 8}}{\text{Stnd Area Count}}$$

8. METHOD SENSITIVITY AND PRECISION

Method sensitivity and precision are outlined in Table 1. The data was generated using standards.

9. DESORPTION EFFICIENCIES AND SAMPLE STABILITY

Desorption efficiencies and sample stability data is listed in Table 2.

TABLE 1
METHOD SENSITIVITY AND PRECISION FOR BROMOXYNIL

CONCENTRATION, UG/ML	AREA COUNT	RELATIVE STND. DEV. n=4
1.0 ug/ml	16.234	5.2 %
0.5 ug/ml	8.112	4.4 %
0.1 ug/ml	1.579	8.0 %
0.02 ug/ml	0.322	8.8 %

Correlation coefficient: 0.999 Slope: 0.0615 ug/ml/ AC
Intercept: 0.0014 ug/ml LOD : 0.0020 ug/ml (0.016 ug/sample)

TABLE 2
DESORPTION EFFICIENCIES AND STORAGE STABILITY

BROMOXYNIL, UG/SAMPLE*	RECOVERED(n=3)	RECOVERED AFTER 7 DAYS(n=3)
2.0 ug/sample	1.86 (93%)	1.91 (96%)
1.0 ug/sample	0.88 (88%)	0.92 (92%)
0.4 ug/sample	0.38 (95%)	0.36 (90%)

*Note: Bromoxynil was spiked onto the primary section of XAD-2 tubes using microliter syringes and allowed to equilibrate for 1 hour. Three tubes were analyzed immediately; three tubes were stored at -4 C for seven days and then analyzed.

APPENDIX IV.

State of California

M E M O R A N D U M

To : George Lew, Chief
Engineering Evaluation Branch

Date : September 17, 1992

Subject : Bromoxymil
Monitoring Audit

Tom Pomakz
For Alice Westerinen

Alice Westerinen, Manager
Quality Assurance Section
From : Air Resources Board

Please find attached a draft Quality Assurance audit report on the Bromoxymil monitoring project conducted by the Air Resources Board's Engineering Evaluation Branch and Northern Laboratory Branch in January of 1992. The report consists of the results of a flow rate audit of the air samplers, and an analytical performance audit.

Please review the report and feel free to comment on any areas that may need further discussion. We would like to receive your comments by Friday, September 25, 1992.

If you have any questions, please contact Gabriel Ruiz of my staff at 327-0885.

Attachment

cc: Gabriel Ruiz

September 17, 1992

AUDIT REPORT

BROMOXYNIL MONITORING IN IMPERIAL COUNTY

SUMMARY

In January of 1992, the California Air Resources Board's Engineering Evaluation Branch conducted ambient air sampling for Bromoxynil in Imperial County, California. The samples were analyzed by the Air Resources Board's Northern Laboratory Branch.

On January 21, staff of the Quality Assurance Section of the Air Resources Board conducted flow rate audits of the air samplers used by the Engineering Evaluation Branch in the monitoring of Bromoxynil. The audits were conducted with a NIST traceable mass flow meter. The difference between the reported and true flow rates averaged 0.6% with a range of -2.6% to 5.1%.

On February 13, seven samples spiked with known amounts of Bromoxynil were submitted to the laboratory for analysis. The samples were prepared from a 99% pure Bromoxynil sample obtained from Chem Service. The difference between the assigned and the reported Bromoxynil mass averaged -11.2% and ranged from -39.0% to 20.0%.

AUDIT REPORT

BROMOXYNIL MONITORING IN IMPERIAL COUNTY

INTRODUCTION

In January of 1992, the California Air Resources Board's (ARB) Engineering Evaluation Branch (EEB) conducted ambient air sampling for Bromoxynil in Imperial County, California. Ambient air was passed at measured rates through XAD-2 resin adsorbant tubes during several days surrounding an application. The samples were later analyzed by the ARB's Northern Laboratory Branch (NLB). Gabriel Ruiz of the ARB's Quality Assurance (QA) Section conducted a flow rate audit of the air samplers and a performance audit of the laboratory method for the analysis of Bromoxynil.

FLOW RATE AUDIT

On January 21, 1992, a flow rate audit of the four air samplers used by the EEB in the monitoring of Bromoxynil was conducted at the EEB's shop in Sacramento, before the samplers were deployed in the field.

Each sampling apparatus consisted of two XAD-2 resin adsorbant tubes, each connected with Teflon tubing to a rotameter, which was then connected with latex tubing to a double-headed pump, so that the flows did not interfere with each other. The sampling assembly was supported with a two meter section of aluminum tubing. The adsorbant tubes were covered with a plastic hood to protect them from sunlight.

Don Fitzell of the EEB calibrated the samplers by adjusting the valve on the rotameter so that the indicated flow rate was 2.0 liters per minute (lpm). The actual flow was then measured with a bubble meter, and the average of the flow rates measured for all five samplers was reported as the sample collection flow rate.

After the calibration, the flow rate of each sampler was audited with a NIST traceable 3 lpm Matheson mass flow meter (MFM), following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged 0.6% and ranged from -2.6% to 5.1% (Table 1).

Table 1. Results of the flow rate audits of the air samplers used in the monitoring of Bromoxynil.

Sampler	Rotameter	Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
1	1A	2.0	1.86	1.81	2.8
	1B	2.0	1.86	1.77	5.1
5	5A	2.0	1.86	1.85	0.5
	5B	2.0	1.86	1.85	0.5
6	6A	2.0	1.86	1.91	-2.6
	6B	2.0	1.86	1.90	-2.1
9	9A	2.0	1.86	1.85	0.5
	9B	2.0	1.86	1.86	0

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

LABORATORY AUDIT

The accuracy of the NLB's analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with known amounts of Bromoxynil. The samples were prepared and delivered to the laboratory on February 13, 1992, following the procedures outlined in Attachment II, from a 99% pure Bromoxynil sample obtained from Chem Service. The samples were stored in a freezer, along with the ambient monitoring samples, for several days before being extracted. The extracts were then stored until late May before analysis.

The difference between the assigned and the reported Bromoxynil mass for the samples averaged -11.2% and ranged from -39.0% to 20.0%. The results of duplicate samples B1 and B4, and B5 and B7 indicate a moderate degree of precision for the method (Table 2).

Table 2. Results of NLB's analyses of Bromoxynil audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
B1	1.99	1.81	- 9.0
B2	0.50	0.60	20.0
B3	0	ND	N/A
B4	1.99	1.80	- 9.5
B5	1.00	0.95	- 5.0
B6	3.98	3.00	-24.6
B7	1.00	0.61	-39.0

ND = Not Detected

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

Flow Audit Procedure for Air Samplers Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable Brooks automatic flow calibrator. The audit device is placed in series with the sampler's inlet and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fitting.
5. 1/4" to 5/16" Teflon union.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the teflon tubing to the outlet port of the audit device with the Swagelock fitting.
3. Connect the free end of the teflon tubing to the sampler inlet with the Teflon union.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

Performance Audit Procedure
For The Laboratory Analysis Of Bromoxynil

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Bromoxynil. The audit is conducted by submitting audit samples prepared by spiking adsorbant tubes with known concentrations of Bromoxynil. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Bromoxynil, 99% pure, Chem Service Lot #60-80R.
2. Toluene, high purity.
3. XAD-2 resin Adsorbant Tubes
4. 50 ul Microsyringe

Safety Precautions

Bromoxynil may be harmful if inhaled or absorbed through the skin. Can be irritating to mucous membranes. Can cause skin irritation. Avoid direct physical contact. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Standards Preparation

2.5 mg/ml Bromoxynil Stock Solution: Weigh about 25 mg of Bromoxynil into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

5 mg/ml Bromoxynil Stock Solution: Weigh about 50 mg of Bromoxynil into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

0.05 mg/ml Bromoxynil Spiking Solution: Transfer 200 ul of the 2.5 mg/ml Bromoxynil stock solution into a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

0.1 mg/ml Bromoxynil Spiking Solution: Transfer 200 ul of the 5.0 mg/ml Bromoxynil stock solution to a clean 10 ml volumetric flask and dilute with toluene to the mark. Record the concentration.

Sample Preparation

Prepare seven audit samples from the Bromoxynil spiking solutions according to the following table:

Sample	0.05 mg/ml Bromoxynil Volume (ul)	0.1 mg/ml Bromoxynil Volume (ul)
1	40	0
2	10	0
3	0	0
4	0	20
5	20	0
6	0	40
7	0	10

1. Break off the inlet end of the sample tube.

2. Insert the syringe needle into the adsorbant bed of the primary section of the tube, and slowly inject the appropriate volume of Bromoxynil solution. Do not allow the liquid to run down the sides of the tube.

3. Cap the open end of the tube with the plastic cap provided.

4. Label each tube with its assigned number and store in a freezer until ready for analysis.

Table 1A

2nd Quarter, 1992
Toxics Performance Audit Summary
California Air Resources Board
Monitoring and Laboratory Division
Quality Assurance Section

CYL # AAL-20240

Compound	National Institute of Standards and Technology	Laboratory A				Laboratory B			
	Assigned Concentration (ppb)	Meas. Conc. (ppb)	Std. Dev. (ppb)	No. Runs	% Bias	Meas. Conc. (ppb)	Std. Dev. (ppb)	No. Runs	% Bias
Chloroform	---	---	---	---	---	---	---	---	---
Carbon Tetrachloride	---	---	---	---	---	---	---	---	---
Trichloroethene	---	---	---	---	---	---	---	---	---
Tetrachloroethene	---	---	---	---	---	---	---	---	---
Bromomethane	---	---	---	---	---	---	---	---	---
Dichloromethane	---	---	---	---	---	---	---	---	---
1,2-Dichloroethane	---	---	---	---	---	---	---	---	---
1,1,1-Trichloroethane	---	---	---	---	---	---	---	---	---
1,2-Dibromoethane	---	---	---	---	---	---	---	---	---
1,2-Dichloropropane	---	---	---	---	---	---	---	---	---
1,3-Butadiene	---	---	---	---	---	---	---	---	---
Vinyl Chloride	---	---	---	---	---	---	---	---	---
Isoprene	---	---	---	---	---	---	---	---	---
Benzene	7.7	7.8	0.096	4	1.3	7.2	0.2	3	-6.5
Toluene	7.3	7.2	0.082	4	-1.4	7.1	0.2	4	-2.7
o-Xylene	8.3	N/A	---	---	---	6.8	0.1	4	-18.1
m-Xylene	8.0	N/A	---	---	---	6.4	0.1	4	-20.0
p-Xylene	7.6	N/A	---	---	---	6.1	0.1	4	-19.7
Chlorobenzene	---	---	---	---	---	<0.1	---	4	--- *
1,2-Dichlorobenzene	---	---	---	---	---	<0.2	---	4	--- *
1,3-Dichlorobenzene	---	---	---	---	---	<0.1	---	4	--- *
Ethylbenzene	---	---	---	---	---	<0.5	---	4	--- *
Styrene	---	---	---	---	---	<0.1	---	4	--- *
Dichlorodifluoromethane	---	---	---	---	---	---	---	---	---
Trichlorofluoromethane	---	---	---	---	---	---	---	---	---
Trichlorotrifluoroethane	---	---	---	---	---	---	---	---	---

* Compound not present in the original mixture.

N/A = Not Analyzed

Percent Bias = (Measured Concentration - Assigned Concentration)/Assigned Concentration X 100

ARB Northern Laboratory Branch analysis values reflect concentration assignments of the laboratory working standards made by comparison to NIST reference materials received 4/90.

MLD/QA 9/92

Table 1B

2nd Quarter, 1992
Toxics Performance Audit Summary
California Air Resources Board
Monitoring and Laboratory Division
Quality Assurance Section

CYL # AAL-20240

Compound	National Institute of Standards and Technology	Laboratory C				
	Assigned Concentration (ppb)	Meas. Conc. (ppb)	Std. Dev. (ppb)	No. Runs	% Bias	
Chloroform	---	---	---	---	---	
Carbon Tetrachloride	---	---	---	---	---	
Trichloroethene	---	---	---	---	---	
Tetrachloroethene	---	---	---	---	---	
Bromomethane	---	---	---	---	---	
Dichloromethane	---	---	---	---	---	
1,2-Dichloroethane	---	---	---	---	---	
1,1,1-Trichloroethane	---	---	---	---	---	
1,2-Dibromoethane	---	---	---	---	---	
1,2-Dichloropropane	---	---	---	---	---	
1,3-Butadiene	---	---	---	---	---	
Vinyl Chloride	---	---	---	---	---	
Isoprene	---	---	---	---	---	
Benzene	7.7	6.6	N/R	4	-14.3	
Toluene	7.3	6.6	N/R	4	-9.6	
o-Xylene	8.3	7.2	N/R	4	-13.3	
m-Xylene + p-Xylene	15.6	11.6	N/R	4	-25.6	**
Chlorobenzene	---	---	---	---	---	
1,2-Dichlorobenzene	---	---	---	---	---	
1,3-Dichlorobenzene	---	---	---	---	---	
Ethylbenzene	---	---	---	---	---	
Styrene	---	---	---	---	---	
Dichlorodifluoromethane	---	---	---	---	---	
Trichlorofluoromethane	---	---	---	---	---	
Trichlorotrifluoroethane	---	---	---	---	---	

** m- and p-xylene coeluted. Cylinder concentration of m-xylene = 8.0 ppb, p-xylene = 7.6 ppb.

N/R = Not Reported

Percent Bias = (Measured Concentration - Assigned Concentration)/Assigned Concentration X 100

ARB Northern Laboratory Branch analysis values reflect concentration assignments of the laboratory working standards made by comparison to NIST reference materials received 4/90.

MLD/QA 9/92